

PATENT ABSTRACTS OF JAPAN

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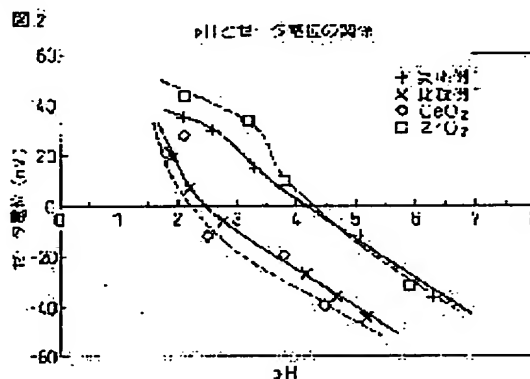
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(54) CERIUM-ZIRCONIUM COMPOUND METALLIC OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cerium-zirconium compound oxide having improved durability at high temperature and stable OSC (oxygen storage capacity) performance.

SOLUTION: The cerium-zirconium compound metallic oxide has at least 85% of the total mole number of Ce and Zr with respect to the whole metal mole number in the compound metallic oxide, 1/9 to 9/1 molar ratio of Ce/Zr and over 3.5 isoelectric point of the compound metallic oxide. Preferably the compound metallic oxide has 3/7 to 7/3 molar ratio of Ce/Zr and 3.8 to 5.0 isoelectric point and contains rare earth metals (excluding Ce) by <15 mol% with respect to the total metal mole number in the material. The cerium- zirconium compound metallic oxide contains CeO₂ as nuclei and ZrO₂ present around the nuclei.



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CLAIMS

[Claim(s)]

[Claim 1] The cerium-zirconium compound metallic oxide which it is a cerium-zirconium compound metallic oxide, and the number of sum total mols of Ce and Zr is at least 85% on the basis of the total number of metal mols in said compound metallic oxide, and the mole ratios of Ce/Zr are 1 / 9 - 9/1, and is characterized by the isoelectric point of said compound metallic oxide exceeding 3.5.

[Claim 2] The cerium-zirconium compound metallic oxide according to claim 1 said whose isoelectric points the mole ratios of said Ce/Zr are 3 / 7 - 7/3, and are 3.8-5.0.

[Claim 3] The cerium-zirconium compound metallic oxide according to claim 1 or 2 which contains a rare earth metal (except for Ce) less than [15 mol %] on the basis of the total number of metal mols in said compound metallic material.

[Claim 4] The cerium-zirconium compound metallic oxide which is a cerium-zirconium compound metallic oxide, the number of sum total mols of Ce and Zr is at least 85%, uses CeO₂ as a nucleus on the basis of the total number of metal mols in said compound metallic oxide, and is characterized by ZrO₂ existing in the surroundings of the nucleus.

[Claim 5] The cerium-zirconium compound metallic oxide according to claim 4 which has the diameter said whose nucleus of CeO₂ is 5-20nm.

[Claim 6] The catalyst for exhaust gas purification characterized by noble metals being supported by the cerium-zirconium compound metallic oxide given in any 1 term of claims 1-5.

[Claim 7] The synthetic approach of the cerium-zirconium compound metallic oxide according to claim 1 or 4 characterized by drying and calcinating after mixing a ceria sol and a zirconium compound solution, or a zirconia sol and preparing suspension.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] About a cerium-zirconium compound metallic oxide, this invention is divided and relates to the cerium-zirconium compound metallic oxide suitable for being used for an internal combustion engine's catalyst for exhaust gas purification as a co-catalyst.

[0002]

[Description of the Prior Art] Although nitrogen oxides (NOX), a carbon monoxide (CO), a hydrocarbon (HC), etc. are contained in the exhaust gas discharged by internal combustion engines, such as car motor, while oxidizing CO and HC, the three way component catalyst which returns NOX to O₂ can purify such harmful matter. Generally this three way component catalyst supports the catalyst component of noble metals, such as platinum (Pt), palladium (Pd), and a rhodium (Rh), to the support of oxides, such as gamma-alumina, and is constituted.

[0003] In order for oxidation of CO and HC and reduction of NOX to advance efficiently in such a three way component catalyst, it is required to control an internal combustion engine's air-fuel ratio appropriately, and for the specific narrow range to have an exhaust gas presentation. However, it may happen to change an exhaust gas presentation to some extent, and to separate from the specific narrow range by the time lag of a control system etc., in fact.

[0004] Here, a cerium-zirconium multiple oxide can produce a valence change trivalent and tetravalent in Ce atom contained. And according to the oxidizing atmosphere containing comparatively many O₂, the oxygen occlusion ability (OSC) of Ce atom producing valence change from trivalent in tetravalence, absorbing oxygen, and Ce atom producing valence change from tetravalence in trivalent in the reducing atmosphere containing comparatively many COs and HC, and emitting oxygen can be demonstrated. Therefore, if a cerium-zirconium multiple oxide is included in the catalyst for exhaust gas purification, fluctuation of an exhaust gas presentation [/ near the catalyst component] is eased, and the above-mentioned exhaust gas purification can be advanced more efficiently.

[0005] In addition, since remarkable generation of heat arises in connection with the oxygen uptake of a cerium-zirconium multiple oxide, this generation of heat can be used for warming up of the catalyst at the time of engine starting, and the initiation stage of catalytic activity can be brought forward. For this reason, the cerium-zirconium multiple oxide is used as a co-catalyst of the catalyst for exhaust gas purification. There are JP,10-194742,A, JP,6-279027,A, etc. as advanced technology of this cerium-zirconium multiple oxide.

[0006]

[Problem(s) to be Solved by the Invention] However, generally, when such a cerium-zirconium multiple oxide is put to elevated temperature about 1000 degrees C or more for a long period of time, it causes the fall of OSC ability and has the problem that endurance is not enough. Therefore, the endurance under an elevated temperature is improved and this invention aims at offering the cerium-zirconium multiple oxide which has the stable OSC ability.

[0007]

[Means for Solving the Problem] The above-mentioned purpose is attained by the cerium-zirconium compound metallic oxide which it is a cerium-zirconium compound metallic oxide, and the number of sum total mols of Ce and Zr is at least 85% on the basis of the total number of metal mols in said

compound metallic material, and the mole ratios of Ce/Zr are 1 / 9 - 9/1, and is characterized by the isoelectric point of said compound metallic oxide exceeding 3.5.

[0008] That is, this invention is a cerium-zirconium compound metallic oxide which has a specific presentation, and is a cerium-zirconium compound metallic oxide characterized by having the isoelectric point which divides and exceeds 3.5.

[0009] This "isoelectric point" is a characteristic value measured based on the electrophoresis of the particle in a slurry, in the approach of specifying by this invention, the isoelectric point of CeO₂ is 2.4 and the isoelectric point of ZrO₂ is 4.0. That is, the cerium-zirconium compound metallic oxide of this invention is characterized by having the isoelectric point near ZrO₂, including the both sides of CeO₂ and ZrO₂.

[0010] As this isoelectric point, the cerium-zirconium compound metallic oxide of this invention has a value with the presentation of CeO₂ and ZrO₂ notably higher than the cerium-zirconium compound metallic oxide of the equivalent conventional technique. Moreover, the endurance ability of the catalyst for exhaust gas purification which comes to support Pt to this cerium-zirconium compound metallic oxide is improved more notably than that of the conventional technique.

[0011] It is thought that especially such a condition is stabilized when the little element with which the particle from which the cerium-zirconium compound metallic oxide of this invention constitutes it presented a condition [mainly like / ZrO₂ and the inside / drawing 1 which mainly consists of CeO₂] whose outside is, and was chosen as ZrO₂ from the rare earth metal lives together from these things. That is, in another aspect of affairs, this invention is a cerium-zirconium compound metallic oxide, and is a cerium-zirconium compound metallic oxide which the number of sum total mols of Ce and Zr is at least 85%, uses CeO₂ as a nucleus on the basis of the total number of metal mols in said compound metallic oxide, and is characterized by ZrO₂ existing in the surroundings of the nucleus.

[0012] When ZrO₂ and CeO₂ present such an existence gestalt, heat-resistant high ZrO₂ holds the gestalt of the particle of a cerium-zirconium compound metallic oxide, and that to which CeO₂-ZrO₂ of the border area of a CeO₂ and/or the inside inside, and an inside outside is stabilized with time, and can demonstrate OSC ability by it is presumed. In addition, drawing 1 is an explanatory view strictly like a model, and does not limit this invention.

[0013]

[Embodiment of the Invention] This invention is a cerium-zirconium compound metallic oxide. On the basis of the total number of metal mols in said compound metallic oxide The number of sum total mols of Ce and Zr is at least 85%, and the mole ratios of Ce/Zr are 1 / 9 - 9/1. And it is characterized by the isoelectric point of said compound metallic oxide exceeding 3.5, and more preferably, the mole ratios of said Ce/Zr are 3 / 7 - 7/3, and said isoelectric points are 3.8-5.0. In this invention, the "isoelectric point" is defined as the value measured by JIS R1638 with the stopwatch method which is one of the electrophoresis microscopic methods of a publication.

[0014] Moreover, a "cerium-zirconium compound metallic oxide" is an oxide which can contain still more nearly another "metal" including Ce and Zr at least. Another "metal" can be broadly chosen as this pan from s-block metal, d-block metal, p-block metal, and f-block metal. Specifically Sodium (Na), a potassium (K), magnesium (Mg), calcium (calcium), Barium (Ba), strontium (Sr), a lanthanum (La), an yttrium (Y), A cerium (Ce), PURASEOJIUMU (Pr), neodymium (Nd), samarium (Sm), A europium (Eu), a gadolinium (Gd), titanium (Ti), tin (Sn), A zirconium (Zr), manganese (Mn), iron (Fe), cobalt (Co), They can be nickel (nickel), chromium (Cr), niobium (Nb), copper (Cu), vanadium (V), molybdenum (Mo), a tungsten (W), zinc (Zn), aluminum (aluminum), silicon (Si), a tantalum (Ta), etc.

[0015] Preferably, the still more nearly another above-mentioned "metal" is at least one sort of rare earth metals, such as La, Y, Ce, Pr, Nd, Sm, Eu, and Gd, and is contained in the amount below 15 mol % on the basis of the total number of metal mols in a cerium-zirconium compound metallic oxide. When "metals" is these rare earth metals, it is thought that especially ZrO₂ [of a nucleus] of the surroundings is stabilized.

[0016] This cerium-zirconium compound metallic oxide can be obtained by drying and calcinating, after being manufactured using a ceria sol as a source of a cerium, mixing the metallic-compounds solution or sol of a ceria sol and a zirconium compound solution or a zirconia sol, and desirable still

more nearly another "metal" at a predetermined rate preferably and preparing suspension.

[0017] Here, "sols", such as a "ceria sol" and a "zirconia sol", is colloid of the oxide of a liquid especially distributed in water, or a hydrate, the matter which calcinates and generates metallic oxides, such as Ceria and a zirconia, is meant, and, specifically, the matter obtained by hydrolysis etc. carrying out alkoxides, such as a cerium or a zirconium, acetylacetonate, acetate, a nitrate, etc. in a solution is illustrated. Moreover, the water solution of oxy-zirconium-nitrate $ZrO(NO_3) \cdot 2.2H_2O$ and zirconium chloride $ZrCl_4$ grade is illustrated by the "zirconium compound solution."

[0018] The conditions heated in a 600-900-degree C atmospheric-air ambient atmosphere for several hours are suitable for baking. Thus, after presenting a grinding process with the obtained cerium-zirconium compound metallic oxide as occasion demands, noble metals, such as platinum, palladium, and a rhodium, can be supported and the catalyst for exhaust gas purification can be prepared. Even if this catalyst for exhaust gas purification is put to the temperature of about 1000 degrees C, it can demonstrate the stable high exhaust gas purification engine performance, without OSC ability deteriorating intentionally. Hereafter, an example explains this invention more concretely.

[0019]

[Example] The solution which made 100g ion exchange water dissolve the oxy-zirconium nitrate of 41.16 g and a 6.48g nitric-acid yttrium in the ceria sol (15 mass %, the Taki Chemical make, knee DORARU U-15 as CeO_2) of a 1193.33 g example was added and stirred, and uniform suspension was created.

After presenting heating of 120 degree-Cx 24 hours with this suspension and evaporating water, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of following this invention of presentation (mass ratio): $CeO_2/ZrO_2/Y_2O_3=58/38/4$ was obtained.

[0020] Subsequently, 300g ion exchange water was made to distribute 50g of this multiple oxide, the slurry was created, 11.36g (Pt concentration 4.4 mass %) of water solutions of a dinitrodiammine platinum complex was added to this slurry, and it stirred for 2 hours. Subsequently, after presenting heating of 120 degree-Cx 24 hours with this slurry and evaporating water, baking of 500 degree-Cx 2 hours was presented, and the catalyst for exhaust gas purification of this invention which supported Pt of 1 mass % to the cerium-zirconium content multiple oxide of this invention was acquired.

[0021] 95g added, the solution which made 50g ion exchange water dissolve a 6.48g nitric-acid yttrium in the above-mentioned ceria sol of a 2193.33 g example, and the zirconia sol (20 mass %, the product made from the first rare element chemical industry, zirconia (HA) as ZrO_2) were stirred, and uniform suspension was created.

[0022] Subsequently, like the example 1, after evaporating water from this suspension, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of following this invention of presentation (mass ratio): $CeO_2/ZrO_2/Y_2O_3=58/38/4$ was obtained. Subsequently, like the example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of this invention was acquired.

[0023] 154.5g addition was carried out, the solution which made 50g ion exchange water dissolve a 6.48g nitric-acid yttrium in the above-mentioned ceria sol of a 3193.33 g example, and the zirconia sol (12.5 mass %, the first rare element chemical industry, the zirconia (AC) 7 as ZrO_2) were stirred, and uniform suspension was created.

[0024] Subsequently, like the example 1, after evaporating water from this suspension, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of following this invention of presentation (mass ratio): $CeO_2/ZrO_2/Y_2O_3=58/38/4$ was obtained. Subsequently, like the example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of this invention was acquired.

[0025] To the above-mentioned ceria sol of a 4193.33 g example, the oxy-zirconium nitrate of 34.66 g, the 3.99g lanthanum nitrate, and the solution that dissolved 8.94g nitric-acid PURASEOJIUMU were added and stirred to 300g ion exchange water, and uniform suspension was created.

[0026] Subsequently, like the example 1, after evaporating water from suspension, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of following this invention of presentation (mass ratio): $CeO_2/ZrO_2/La_2O_3/Pr_6O_{11}=58/32/3/7$ was obtained. Subsequently, like the example 1, Pt of 1 mass % was supported to this multiple oxide using the

dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of this invention was acquired.

[0027] The solution made to dissolve a 73.165g cerium nitrate, a 41.16g oxy-zirconium nitrate, and a 6.48g nitric-acid yttrium in ion exchange water of 1500g of examples of a comparison was created. Subsequently, aqueous ammonia with a concentration of one mol [l.] was dropped at this solution, pH was adjusted to about 9, and precipitate was produced according to coprecipitation.

[0028] Subsequently, after evaporating water from the solution containing this precipitate like an example 1, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of the following example of a comparison of presentation (mass ratio):CeO₂/ZrO₂/Y₂O₃=58/38/4 was obtained. Subsequently, like the example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of the example of a comparison was acquired.

[0029] The solution made to dissolve a 73.17g cerium nitrate, a 34.66g oxy-zirconium nitrate, a 3.99g lanthanum nitrate, and 8.94g nitric-acid PURASEOJIUMU in ion exchange water of 2500g of examples of a comparison was prepared. Subsequently, after producing precipitate from this solution according to coprecipitation and evaporating water like the example 1 of a comparison, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of the following example of a comparison of presentation (mass ratio):CeO₂/ZrO₂/La₂O₃/Pr₆O₁₁=58/32/3/7 was obtained. Subsequently, like the example 1, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of the example of a comparison was acquired.

[0030] Ion exchange water of 3500g of examples of a comparison was made to distribute 29g cerium oxide powder, subsequently to 200g ion exchange water the solution in which the 41.16g oxy-zirconium nitrate and the 6.48g nitric-acid yttrium were dissolved was added and stirred, and the slurry was prepared. Subsequently, aqueous ammonia was dropped at this slurry like the example 1 of a comparison, pH was adjusted to about 9, and the precipitate containing a zirconium and an yttrium was produced.

[0031] Subsequently, after evaporating water, baking of 700 degree-Cx 5 hours was presented, and the cerium-zirconium compound metallic oxide of the following example of a comparison of presentation (mass ratio):CeO₂/ZrO₂/Y₂O₃=58/38/4 was obtained. Subsequently, like the example 1 of a comparison, Pt of 1 mass % was supported to this multiple oxide using the dinitrodiammine platinum complex, and the catalyst for exhaust gas purification of the example of a comparison was acquired.

[0032] - About each cerium-zirconium compound metallic oxide of the measurement-examples 1-4 of the isoelectric point, and the examples 1-3 of a comparison, the isoelectric point was measured according to the stopwatch method which is one of the electric ***** fine mirror methods of a publication to JIS R1638. This result is collectively shown in Table 1. Moreover, the relation of the pH and F-potential which were measured in order to ask drawing 2 for the isoelectric point in the above-mentioned measuring method about the cerium-zirconium compound metallic oxide of an example 1 and the example 1 of a comparison and CeO₂ powder, and ZrO₂ powder is shown.

[0033] It turns out that there is a difference clear to the isoelectric point of the cerium-zirconium compound metallic oxide of an example and the example of a comparison from these results, an example shows the isoelectric point near ZrO₂ powder, and the isoelectric point near CeO₂ powder is shown in the example of a comparison. however, in examples 1-3, the examples 1 and 3 of a comparison and an example 4, and the example 2 of a comparison Since the presentation of a cerium-zirconium compound metallic oxide is equivalent, these differences It is judged as the thing originating in a CeO₂ and ZrO₂ existence gestalt, and in the example, since ZrO₂ exists in the surroundings of it by using CeO₂ as a nucleus as shown in drawing 1 , it is thought that the isoelectric point near ZrO₂ powder is shown.

<TXF FR=0002 HE=095 WI=080 LX=1100 LY=0300> [0034] - Each catalyst for exhaust gas purification of the catalyst performance-evaluation-examples 1-4 and the examples 1-3 of a comparison was compressed and cracked, and the catalyst engine performance was evaluated about 2.0g each made into the pellet with a diameter of about 2mm. In order to grasp the amelioration effectiveness of endurance, after presenting durable processing of 1000 degree-Cx 3 hours with each

catalyst for exhaust gas purification, the catalyst engine performance was evaluated.

[0035] Evaluation conditions measured C₃H₆(HC) and the rate of purification of each component of NO and CO, considering as the conditions from which the rich gas/lean gas of the presentation shown in Table 1 change for every minute, and carrying out the temperature up of whenever [catalyst floor temperature] to 400 degrees C the rate for 10-degree-C/so that the difference in OSC ability may appear in a result. The catalyst engine performance made the index temperature by which these components are purified 50%. This result is collectively shown in Table 2.

[0036]

[Effect of the Invention] The endurance under an elevated temperature is improved and the cerium-zirconium multiple oxide which has the stable OSC ability can be offered.

[0037]

[Table 1]

〈表1〉評価用のガス組成

| | N ₂ (%) | CO ₂ (%) | NO (ppm) | CO (%) | C ₃ H ₆ (ppmC) | H ₂ (%) | O ₂ (%) | H ₂ O (%) |
|-------|-----------------------|------------------------|-------------|-----------|-----------------------------------------|-----------------------|-----------------------|-------------------------|
| リッチガス | バランス | 10 | 2200 | 2.80 | 2500 | 0.27 | 0.77 | 10 |
| リーンガス | バランス | 10 | 2200 | 0.81 | 2500 | 0 | 1.7 | 10 |

[0038]

[Table 2]

〈表2〉触媒性能と等電点の測定結果

| | 組 成 | 質量比 | HC | NO | CO | 等電点 |
|------|---------------|-----------|-----|-----|-----|-----|
| 実施例1 | Ce-Zr-Y-O | 58/38/4 | 234 | 266 | 180 | 4.2 |
| 実施例2 | Ce-Zr-Y-O | 58/38/4 | 253 | 286 | 221 | 3.9 |
| 実施例3 | Ce-Zr-Y-O | 58/38/4 | 263 | 301 | 216 | 4.1 |
| 実施例4 | Ce-Zr-La-Pr-O | 58/32/3/7 | 245 | 270 | 201 | 4.0 |
| 比較例1 | Ce-Zr-Y-O | 58/38/4 | 280 | 308 | 242 | 2.5 |
| 比較例2 | Ce-Zr-La-Pr-O | 58/32/3/7 | 269 | 303 | 253 | 2.2 |
| 比較例3 | Ce-Zr-Y-O | 58/38/4 | 302 | 366 | 299 | 3.3 |

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the model Fig. of the cerium-zirconium compound metallic oxide of this invention.

[Drawing 2] It is the graph which shows the relation between pH in measurement of the isoelectric point, and F-potential.

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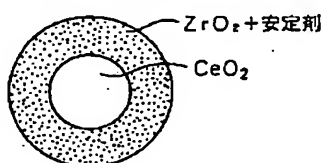
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DRAWINGS

[Drawing 1]

図 1

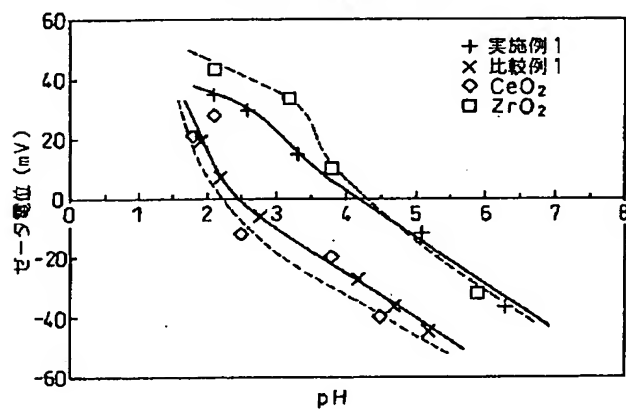
本発明のセリウム-ジルコニウム複合金属酸化物のモデル図



[Drawing 2]

図 2

pHとゼータ電位の関係



[Translation done.]